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(71) Applicant Labofina SA (Belgium), 33 Rue de la Loi, 1040 Bruxelles, Belgium	
(72) Inventors Guy L. G. Debras, Georges E. M. J. de Clippeleir, Raymond M. Cahen	
(74) Agent and/or Address for Service Page White & Farrer, 5 Plough Place, New Fetter Lane, London EC4A 1HY	

(54) **Process for removing carbonyl sulphide from liquid hydro-carbon feedstocks**

(57) A process for the purification of liquid hydrocarbon feedstocks containing propylene and containing from 1 to 70 ppm of COS, consists in passing the feedstock over an absorbent material comprising nickel deposited on a support, the nickel being present in the form of nickel oxide and in the form of metallic nickel, and the quantity of metallic nickel being between 35 to 70% by weight of the total nickel.

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SPECIFICATION

Process for removing carbonyl sulphide from liquid hydrocarbon feedstocks

5 The present invention relates to a process for removing the sulphur, present in the form of carbon oxy-
sulphide or carbonyl sulphide, from liquid hydrocarbons, in particular from hydrocarbon feedstocks con-
taining propylene. 5

In refineries, the treatment of liquid hydrocarbons to remove or convert the impurities therein requires
complex and expensive processes. Various sulphur compounds constitute the usual impurities which it is
10 often desired to remove, the compounds being hydrogen sulphide, mercaptans and, in particular, car-
bonyl sulphide. 10

It is common in industrial practice to reduce the sulphur content by treating the hydrocarbons in the
gaseous state. A widely accepted practice consists in using diethanolamine, diisopropanolamine, mono-
ethanolamine and tetraethylene glycol to remove the sulphides from combustible gases in the gaseous
15 state. It is also known that those solvents can be used to treat hydrocarbons in the liquid state. 15

However, when those solvents are used to extract the impurities from hydrocarbons in the liquid state,
it is not possible to reduce the content of carbonyl sulphide, hereafter referred to as COS for the sake of
simplicity, to less than 5 ppm.

It is also known that recently developed propylene polymerization processes are using increasingly effi-
20 cient catalysts. However, those catalysts are extremely sensitive to all polar impurities such as COS, for
example, which has a dipole moment of 0.736 Debye. When using those polymerization processes, it is
therefore important to purify the feedstock so that the residual content of the impurities is extremely low. 20

With the conventional processes, which treat feedstocks capable of initially containing from 30 to 70
ppm of COS, a residual COS content of from 10 to 20 ppm is achieved after purification.

25 It has already been proposed to treat liquid hydrocarbon feedstocks, containing propylene, with 2-(2-
aminoethoxy)ethanol, known as diglycolamine, in order to remove the COS. However, although the re-
sidual content obtained is low, being of the order of ppm, it is still not sufficient to satisfy the conditions
of polymerizations using very active Ziegler-type catalysts. 25

In addition to the treatment technique using liquid-liquid contact, treatments involving liquid-solid con-
30 tact have also been proposed. 30

Those latter types of treatment have the advantage of restricting the risks of contamination of the pro-
pylene which is subsequently to be polymerized, which contamination would make it necessary to have a
second absorber.

It has already been proposed to use a solid material consisting of a porous inert support having a large
35 specific surface area, such as silica gel, pumice or Mg silicate and oxides of Cd, Zn, Ni and Co, over
which the liquefied feedstock is passed, leading to a residual COS content of less than 1 ppm in the
feedstock. 35

It has also been proposed to use absorbents composed of iron oxide, copper oxide or copper and
chromium oxide on a support of high specific surface area, such as active charcoal or alumina, so as to
40 reduce the COS content of the liquid hydrocarbons from 50 to 60 ppm in the initial feedstock to about 0.5
ppm. 40

However, although that COS content is already very low, it is still not sufficient to allow propylene
which is purified in this way to be sent to a polymerization unit which uses very active Ziegler catalysts.

It has also been proposed to treat the feedstocks by passing them over basic ion exchange resins at
45 ambient temperature. Nevertheless, the residual COS content which is obtained is also of the order of
ppm, which is too high to carry out the polymerization in the presence of the latest generation of poly-
merization catalysts. 45

It has also been proposed to use zinc oxide which has been deposited on an alumina support, but that
type of catalyst is not sufficiently active to be able to remove the COS down to residual contents below
50 30 ppb. 50

Consequently, there is a need for a process which makes it possible to desulphurize liquid hydrocarbon
feedstocks containing propylene and other olefins, and in particular to remove the COS from such feed-
stocks, until the residual COS content does not exceed 30 ppb, so that the new generation of propylene
polymerization catalysts are not poisoned too quickly.

55 The present invention relates to a process for the purification of liquid hydrocarbon feedstocks which
makes it possible to satisfy the above-mentioned criteria. 55

Also, the present invention relates to a purification process which makes it possible to remove the COS
from liquid hydrocarbon feedstocks containing propylene, so that the residual COS content is less than
30 ppb.

60 The purification process of the present invention for removing the COS from liquid hydrocarbon feed-
stocks including propylene and containing from 1 to 70 ppm of COS, comprises passing the liquid hydro-
carbon feedstocks over an absorbent material comprising nickel deposited on a support, the nickel being
present in the form of nickel oxide and in the form of metallic nickel, and the quantity of metallic nickel
being from 35 to 70% by weight of the total nickel. 60

65 It has been found, unexpectedly, that by passing a liquid hydrocarbon feedstock, in the preferred case 65

- a propylene feedstock intended for polymerization, over an absorbent material consisting of from 40 to 70% by weight of nickel deposited on a support representing from 60 to 30% by weight of the absorbent material, the nickel being present to the extent of from 35 to 70% by weight in the form of metallic nickel, the purified feedstock obtained corresponds to the purity conditions required for polymerization in the presence of the latest generation of Ziegler catalyst, i.e. the feedstock has a COS content not exceeding 30 ppb. 5
- Silica, silico-aluminas, alumina, keiseltuhr and other similar materials can be used as the support on which the nickel is deposited.
- The nickel can be deposited on the support by any of the methods which are well known to those skilled in the art, for example by dissolving nickel nitrate in water, mixing the solution with the support and precipitating the nickel, for example in the form of nickel carbonate, and then washing, drying and calcining the precipitate. The nickel deposited in this way is then partially reduced by means of hydrogen so as to form metallic nickel in a quantity of from 35 to 70% of the total quantity of nickel deposited, the remainder being in the form of nickel oxide. 10
- In general, the size of the nickel crystallites after reduction is from 10 to 200Å. The size of the nickel crystallites depends inter alia on the degree of reduction which is carried out. In fact, if the degree of reduction is increased, the size of the crystallites is increased but the absorbent material obtained no longer has such good properties. On the other hand, if the degree of reduction is too low, the crystallites still have good dimensions but the quantity of nickel available in this case is too small to ensure successful purification of the feedstock. 15
- The specific surface area of the absorbent material obtained after reduction is generally from 100 to 200 m²/g.
- The particle size of the absorbent material depends in particular on the pressure loss which is allowed in the reactor. It has been noted, however, that it is advantageous to use the absorbent material in finely divided form. In general, the particle size of the material does not exceed about 3 mm and is most frequently from 1 to 2.5 mm. 20
- In general, the liquid hydrocarbon feedstocks treated contain more than 75% of propylene, more particularly up to from 85 to 99% of propylene, the COS content normally being of the order of from 1 to 10 ppm. If feedstocks having a higher COS content, i.e. up to 500 ppm, are to be treated, they are first subjected to a treatment with an aminated solvent, such as monoethanolamine, so as to reduce the COS content to an appropriate value, i.e. less than 70 ppm. 25
- In one embodiment of the process of the present invention, the liquid hydrocarbon feedstock containing propylene is passed over the absorbent material of the present invention at a temperature generally of from 0°C to 90°C and at a sufficient pressure to keep the medium in the liquid phase.
- The liquid hourly space velocity, or LHSV, at which the feedstock is passed over is generally from 0.1 to 20 and preferably from 0.2 to 15. 30
- The examples which follow are given in order to provide a better illustration of the process of the present invention, but without thereby restricting its scope.
- Example 1* 40
- A liquid hydrocarbon feedstock containing 99% of propylene and having a residual COS content of 2.7 ppm was passed over an absorbent material consisting of 43.3% by weight of silica as the support, on which nickel was deposited, the nickel being present in the form of NiO to the extent of 34 wt % and in the form of metallic Ni to the extent of 22.7 wt %.
- Before reduction, the absorbent material contained about 49% by weight of nickel. 45
- The absorbent material was finely divided so as to give an average particle size of about 1 mm and the specific surface area of the absorbent material was 145 m²/g.
- The feedstock was passed over the absorbent material at ambient temperature, at a sufficient pressure to keep the feedstock in the liquid phase, and at an LHSV of 5.
- A sample of the purified feedstock was taken and the COS content determined. The COS content was 18 ppb. 50
- Example 2*
- Liquid hydrocarbon feedstocks containing 99% of propylene and having different residual COS contents were passed over the same absorbent material as in Example 1. 55
- The nickel containing absorbent material had a nickel content of about 49% by weight. The absorbent material was finely divided so as to give an average particle size of about 1 mm. The specific area of the absorbent material was about 145 m²/g.
- The feedstocks were passed over the nickel containing material under various operating conditions, which are specified in Table 1. 60
- The pressure was 14 bars. As can be seen from the results, the purified feedstocks each had a COS content lower than 30 ppb, even when the feed contains water, which is known to be detrimental.

TABLE I

	LHSV	Temperature of the bed (°C)	H ₂ O content (ppm)	COS in ppm	out ppb	
5	4.95	20	13	1.8	22	5
	5.05	25	8	4.5	20	
	4.8	23	8	3.1	18	
10	9.3	16	14	1.85	15	10
	15.05	15	14	1.3	24	

Example 3

15 Liquid hydrocarbon feedstocks containing 95.6% propylene, 3.8% propane and 0.6% C₄., the water content of each of which was less than 10 ppm, and having different residual COS contents were passed over the same absorbent as described in Examples 1 and 2. This example is given to illustrate the activity of the catalyst over a long period of time. 15

The feedstocks were passed at a pressure of 14 bar over a bed of nickel containing 2 litres of absorbent material.

20 The other operating conditions such as LHSV and the temperature of the bed are specified in Table II. 20

TABLE II

	Day	Temperature of the bed (°C)	LHSV	COS in ppm	out ppb	
25	1	14	9.4	2.8	25	25
	5	9	9.3	1.4	23	
30	12	6	9.7	4.2	21	30
	19	7	9.7	2.55	20	
	25	10	9.7	3.0	11	
	34	7	9.75	1.9	16	
	39	2	9.85	1.85	23	
35	52	9	9.6	0.85	20	35
	58	3	10.15	0.8	22	
	68	11	9.65	2.2	20	
	82	6	9.75	1.95	15	
40	88	1	9.8	0.8	15	40

This example shows that even after 88 days the activity of the catalyst is always very high.

CLAIMS

- 45 1. A process for the purification of a liquid hydrocarbon feedstock including propylene and containing from 1 to 70 ppm of COS, in order to remove the carbonyl sulphide therefrom, which process comprises passing the liquid hydrocarbon feedstock over an absorbent material comprising nickel which is deposited on a support, the nickel being present in the form of nickel oxide and in the form of metallic nickel, and the quantity of metallic nickel being from 35 to 70% by weight of the total nickel content. 45
- 50 2. A process according to Claim 1, wherein the absorbent material consists of from 40 to 70% by weight of nickel which is deposited on the support which constitutes from 60 to 30% by weight of the absorbent material, the nickel being present to the extent of from 35 to 70% by weight in the form of metallic nickel, and the remainder of the nickel being in the form of nickel oxide. 50
- 55 3. A process according to Claim 1 or Claim 2, wherein the specific surface area of the absorbent material is from 100 to 200 m²/g. 55
4. A process according to any one of Claims 1 to 3, wherein the absorbent material is finely divided and the particle size of the absorbent material does not exceed 3 mm.
5. A process according to Claim 4, wherein the particle size of the absorbent material is from 1 to 2.5 mm.
- 60 6. A process according to any foregoing Claim, wherein the liquid hydrocarbon feedstock is passed over the absorbent material at a temperature of from 0°C to 90°C, at a sufficient pressure to keep the feedstock in the liquid phase, and at a liquid hourly space velocity of from 0.1 to 20. 60
7. A process according to Claim 6, wherein the liquid hourly space velocity is from 0.2 to 15.
8. A process according to any foregoing Claim, wherein the liquid hydrocarbon feedstock contains 65 more than 75% propylene. 65

9. A process for the purification of a liquid hydrocarbon feedstock containing more than 95% propylene and containing from 1 to 70 ppm of carbonyl sulphide, in order to remove the carbonyl sulphide therefrom, which process comprises passing the feedstock over an absorbent material consisting of from 40 to 70% by weight of nickel which is deposited on a support which constitutes 60 to 30% by weight of the absorbent material, the nickel being present to the extent of from 35 to 70% by weight in the form of metallic nickel and the remainder of the nickel being in the form of nickel oxide, the absorbent material having a specific surface area of from 100 to 200 m²/g, the feedstock being passed over the absorbent material at a temperature of from 0°C to 90°C and at a sufficient pressure to keep the feedstock in the liquid phase, and at an LHSV of from 0.1 to 20.
10. A process for the purification of a liquid hydrocarbon feedstock substantially as hereinbefore described in any one of Examples 1 to 3.
11. Purified hydrocarbon feedstocks having a low carbonyl sulphide content whenever obtained by a process as claimed in any one of Claims 1 to 10.

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